

**TRANSMISSION X-RAY DIFFRACTION (XRD) PATTERNS RELEVANT TO THE MSL CHEMIN AMORPHOUS COMPONENT: SULFATES AND SILICATES.** R.V. Morris<sup>1</sup>, E.B. Rampe<sup>2</sup>, T.G. Graff<sup>3</sup>, P.D. Archer, Jr.<sup>3</sup>, L. Le<sup>3</sup>, D.W. Ming<sup>1</sup>, and B. Sutter<sup>3</sup>. <sup>1</sup>NASA-JSC, Houston, TX 77058, [richard.v.morris@nasa.gov](mailto:richard.v.morris@nasa.gov). <sup>2</sup>Aerodyne Industries, Jacobs-JETS, Houston, TX 77058, <sup>3</sup>Jacobs, NASA-JSC, Houston, TX 77058.

**Introduction and Background:** The Mars Science Laboratory (MSL) CheMin instrument on the Curiosity rover is a transmission X-ray diffractometer (Co-K $\alpha$  radiation source and a  $\sim 5^\circ$  to  $\sim 52^\circ$   $2\theta$  range) where the analyzed powder samples are constrained to have discrete particle diameters  $<150\ \mu\text{m}$  by a sieve [1]. To date, diffraction patterns have been obtained for one basaltic soil (Rocknest (RN)) and four drill fines of coherent rock (John Klein (JK), Cumberland (CB), Windjana (WJ), and Confidence Hills (CH)) [2-4]. The CheMin instrument has detected and quantified the abundance of both primary igneous (e.g., feldspar, olivine, and pyroxene) and secondary (e.g., Ca-sulfates, hematite, akaganeite, and Fe-saponite) minerals [2-5]. The diffraction patterns of all CheMin samples are also characterized by a broad diffraction band centered near  $30^\circ\ 2\theta$  and by increasing diffraction intensity (scattering continuum) from  $\sim 15^\circ$  to  $\sim 5^\circ$ , the  $2\theta$  minimum.

Both the broad band and the scattering continuum are attributed to the presence of an XRD amorphous component. Estimates of amorphous component abundance, based on the XRD data itself [2,4] and on mass-balance calculations using APXS data crystalline component chemistry derived from XRD data, martian meteorites, and/or stoichiometry [e.g., 6-9], range from  $\sim 20\ \text{wt.}\%$  to  $\sim 50\ \text{wt.}\%$  of bulk sample. The APXS-based calculations show that the amorphous component is rich in volatile elements (esp.  $\text{SO}_3$ ) and is not simply primary basaltic glass, which was used as a surrogate to model the broad band in the RN CheMin pattern [2]. For RN, the entire volatile inventory (except minor anhydrite) is assigned to the amorphous component because no volatile-bearing crystalline phases were reported within detection limits [2]. For JK and CB, Fe-saponite, basanite, and akaganeite are volatile-bearing crystalline components.

Here we report transmission XRD patterns for sulfate and silicate phases relevant to interpretation of MSL-CheMin XRD amorphous components.

**Samples and Methods:** For sulfate experiments, 10 acid-sulfate solutions were prepared from standard reagents (Table 1). Cryoprecipitation (precipitation by removing water as ice) was induced by freezing solutions using liquid  $\text{N}_2$ . After freeze drying, the precipitates were stored in closed containers in a glove box purged with dry- $\text{N}_2$  gas. For silicate experiments, silicate liquids having compositions equivalent to representative MER rocks and soils ( $\text{SO}_3$ - and  $\text{Cl}$ -free) [e.g., 10, 11] were equilibrated at  $1350$ - $1450^\circ\text{C}$  in a 1-atm gas mixing furnace at IW+1 oxygen fugacity and

quenched in water to room temperature. Transmission XRD diffraction patterns were obtained on a CheMin-4 diffractometer which is a laboratory version of the MSL CheMin instrument. Dry  $\text{N}_2$  purge gas was used for the sulfate measurements.

**Table 1.** Compositions of Starting Acid-Sulfate Solutions for Cryoprecipitation of Sulfates

Cation(s)	Concentration (M)	Volume (mL)	Cation Ratio
$\text{Fe}^{3+}$	1.00	20	---
$\text{Fe}^{2+}$	1.00	15	---
$\text{Mg}^{2+}$	1.00	20	---
$\text{Ca}^{2+}$	0.015	500	---
$\text{K}^+$	0.50	40	---
$\text{Na}^+$	0.25	100	---
$\text{Fe}^{2+}, \text{Mg}^{2+}$	0.5, 0.5	20	1:1
$\text{Fe}^{3+}, \text{Mg}^{2+}$	0.5, 0.5	40	1:1
$\text{Fe}^{2+}, \text{Ca}^{2+}$	0.015, 0.015	500	1:1
$\text{Fe}^{3+}, \text{Mg}^{2+}, \text{K}^+, \text{Na}^+$	0.2, 0.2, 0.02, 0.02	100	10:10:1:1

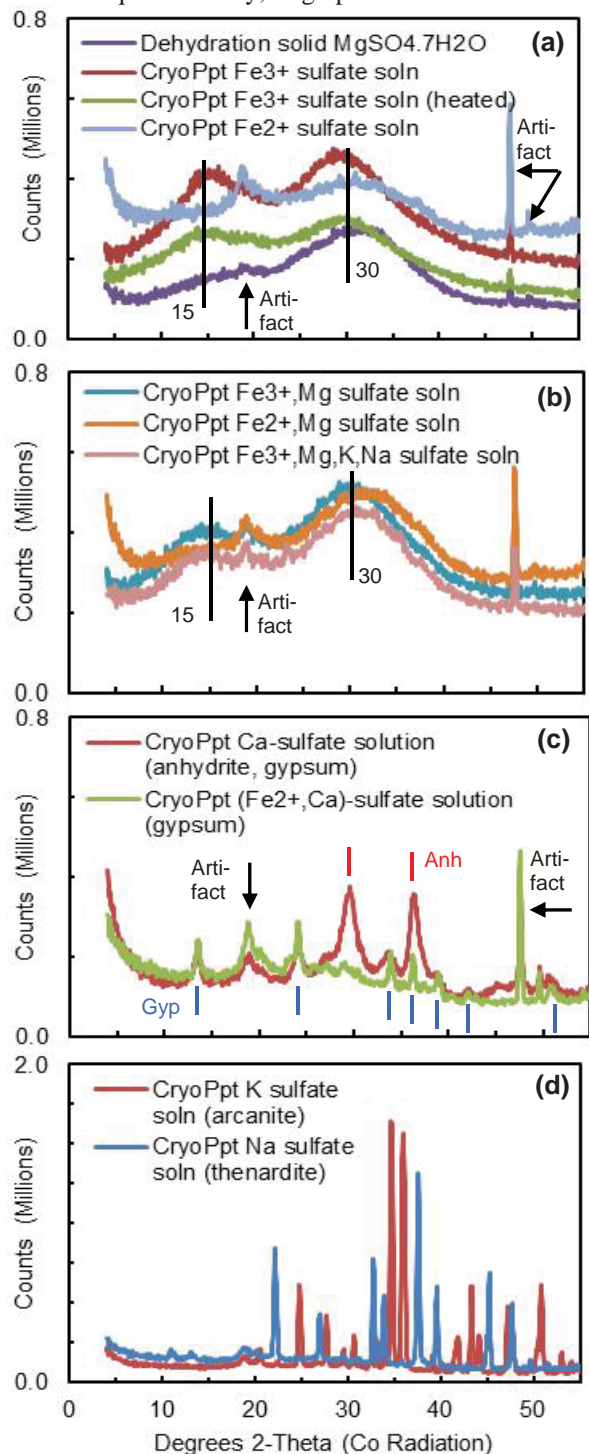
**Results:** Single and mixed cation sulfate solutions of  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  in any proportion are likely capable of forming amorphous products by cryoprecipitation (Fig. 1a,b). Single cation  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  sulfate solutions did not form amorphous precipitates (anhydrite plus gypsum, arcanite, and thenardite, respectively, with gypsum the only hydrated sulfate), and neither did a solution with  $\text{Fe}^{2+}:\text{Ca}^{2+}=1:1$  (Fig. 1c,d), although only gypsum was detected. However, a solution with  $\text{Fe}^{3+}:\text{Mg}^{2+}:\text{Na}^+:\text{K}^+ = 10:10:1:1$  formed an XRD amorphous precipitate (Fig. 1b.). Additional experiments will define the compositions over which mixed cation sulfate solutions produce amorphous and mixed amorphous-crystalline precipitates. Especially relevant are sulfate solutions involving  $\text{Ca}^{2+}$ , because crystalline Ca-sulfates are detected by CheMin [2,4].

In general, amorphous sulfates have a broad intensity maximum near  $\sim 30^\circ\ 2\theta$  and another one with less intensity at lower  $2\theta$  (Fig. 1a,b). Their overall shapes and  $2\theta$  locations (esp.  $\text{Mg}^{2+}$  and/or  $\text{Fe}^{2+}$  compositions) are not inconsistent with CheMin results, e.g., compare with basaltic soil glass (Fig. 2a) which was used by [2] for RN amorphous calculations. However, a quantitative analysis has not been done.

With one exception, the silicate glasses were predominantly amorphous with a single broad diffraction feature whose peak position increased from  $\sim 25^\circ$  to  $\sim 31^\circ\ 2\theta$  with increasing  $\text{SiO}_2$  (Fig. 2a). The Mg-rich composition (Algonquin) produced forsterite plus the most  $\text{SiO}_2$ -poor glass as indicated by the maximum

diffraction intensity at  $\sim 34^\circ 2\theta$  (Fig. 2b). The diffraction pattern of the high-SiO<sub>2</sub> residue of acid-sulfate leached terrestrial basaltic tephra (HWMK051) has a diffraction maximum ( $\sim 26^\circ 2\theta$ ) just longward of that for commercial SiO<sub>2</sub> glass ( $\sim 25^\circ 2\theta$ ) (Fig. 2c).

Our results show that the shape and position of the amorphous component of MSL CheMin data may, at least semiquantitatively, fingerprint its nature.



**References:** [1] Blake et al. (2012) *SSR*, DOI 10.1007/s11214-11012-19905-11211. [2] Bish et al. (2013) *Science*, 341, DOI:10.1126/science.1238932. [3] Blake et al. (2013) *Science*, 341, DOI:10.1126/science.1239505. [4] Vaniman et al., (2013) *Science*, 343 DOI:10.1126/science.1243480. [5] Treiman et al. (2014) *Am. Min.*, 99, 2234. [6] Morris et al. (2013) *LPSC44*, abs. #1653. [7] Morris et al. (2014) *LPSC45*, abs.#1319. [8] Dehouck et al. (2014) *JGR*, 10.1002/2014JE004716. [9] Morris et al. (2015) *LPSC46*, this volume. [10] Ming et al. (2008) *JGR*, 113, E12S39, doi:10.1029/2008JE003195. [11] Morris et al. (2008) *JGR*, 113, E12S42, doi:10.1029/2008JE003201.

**Fig. 1** (left). XRD patterns of cryoprecipitated single and mixed cation acid sulfate solutions and rapid dehydration of solid MgSO<sub>4</sub>·7H<sub>2</sub>O (same as cryoprecipitation).

**Fig. 2** (below). XRD patterns of (a) commercial SiO<sub>2</sub> glass and MER-composition (SO<sub>3</sub>- and Cl-free) silicate liquids quenched from 1350-1450°C and IW+1 oxygen fugacity, (b) similarly quenched Algonquin liquid with olivine and glass, and (c) high-SiO<sub>2</sub> residue of basalt leached under natural acid sulfate conditions (HWKV051) compared to SiO<sub>2</sub> and Adirondack glasses.

